Water Quality and Contaminant Evaluation

at

Union Slough National Wildlife Refuge

1990 and 1991

by

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ABSTRACT

In 1990 sediment and water samples were collected at five outlets in Union Slough National Wildlife Refuge. Forty eight hour sediment bioassay results revealed larval fathead minnow mortality at two of the outlet sites. Water bioassays of the same time frame resulted in no larval fathead minnow mortality at any sampling site. Elevated concentrations of ammonia were the suspected causative agent during this phase of the study.

In 1991 sediment sampling was continued at three of the same five outlet sites. Inorganic analysis of the sediments revealed the presence of eight metals in elevated concentrations. Trace amounts of four polynuclear aromatic hydrocarbons were detected at all three outlets. There were no organochlorine pesticide residues, no organophosphorus pesticides and no chlorophenoxy acid herbicides detected at any site during the sediment analysis. All of the outlet sites had elevated ammonia concentrations. Future studies are proposed to identify background concentrations of agricultural products and agriculture practices in the area, which may affect water quality.

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INTRODUCTION

Established in 1938, Union Slough National Wildlife Refuge (refuge) was created to aid in the production and management of waterfowl in the Mississippi Flyway. The refuge consists of 2200 acres and extends eight miles along Union Slough and Buffalo Creek in Kossuth County, Iowa. The refuge is located along the eastern edge of the Northern Great Plains. The slough itself is a remnant of a pre-glacial riverbed and forms a connection between two watersheds; the Blue Earth River of Minnesota and the East Fork of the Des Moines River of Iowa. The land had been used for agricultural purposes prior to refuge acquisition. Restoration efforts on these lands, initiated shortly after acquisition, have resulted in 1100 acres of refuge wetlands, divided into six separate manageable units.

Concerns regarding agricultural discharges have developed in recent years. The refuge, in conjunction with the Rock Island Field Office (field office), proposed to determine the presence or absence of possible contaminants. The purpose of this study was three fold: 1) identify contaminants in the sediments of three water outlets to Union Slough; 2) quantify concentrations of contamination in the water outlets and 3) identify any additional study needs based on the results. This study was conducted during 1990 and 1991.

METHODS

1990

In June of 1990 grab samples of water and sediment were collected at five outlet sites in the refuge. Individual samples were placed into chemically clean jars and chilled prior to being submitted to the University of Iowa Hygienic Laboratory (IHL) for the performance of 48 hour larval fathead minnow bioassays. With the exception of the Harm's Outlet site, each field sample was split to allow the test to be performed in duplicate with one laboratory control for each sampling location. A field duplicate was taken from the Harm's Outlet site.

IHL analyzed all of the samples at start and end for ammonia nitrogen, total ammonia, unionized ammonia, total hardness, specific conductance (micromhos) and total alkalinity Temperature, dissolved oxygen and pH were monitored at start, 24 hours and 48 hours.

All of the sampling sites were chosen because of their proximity to agricultural enterprises. These businesses include either farming or livestock operations.

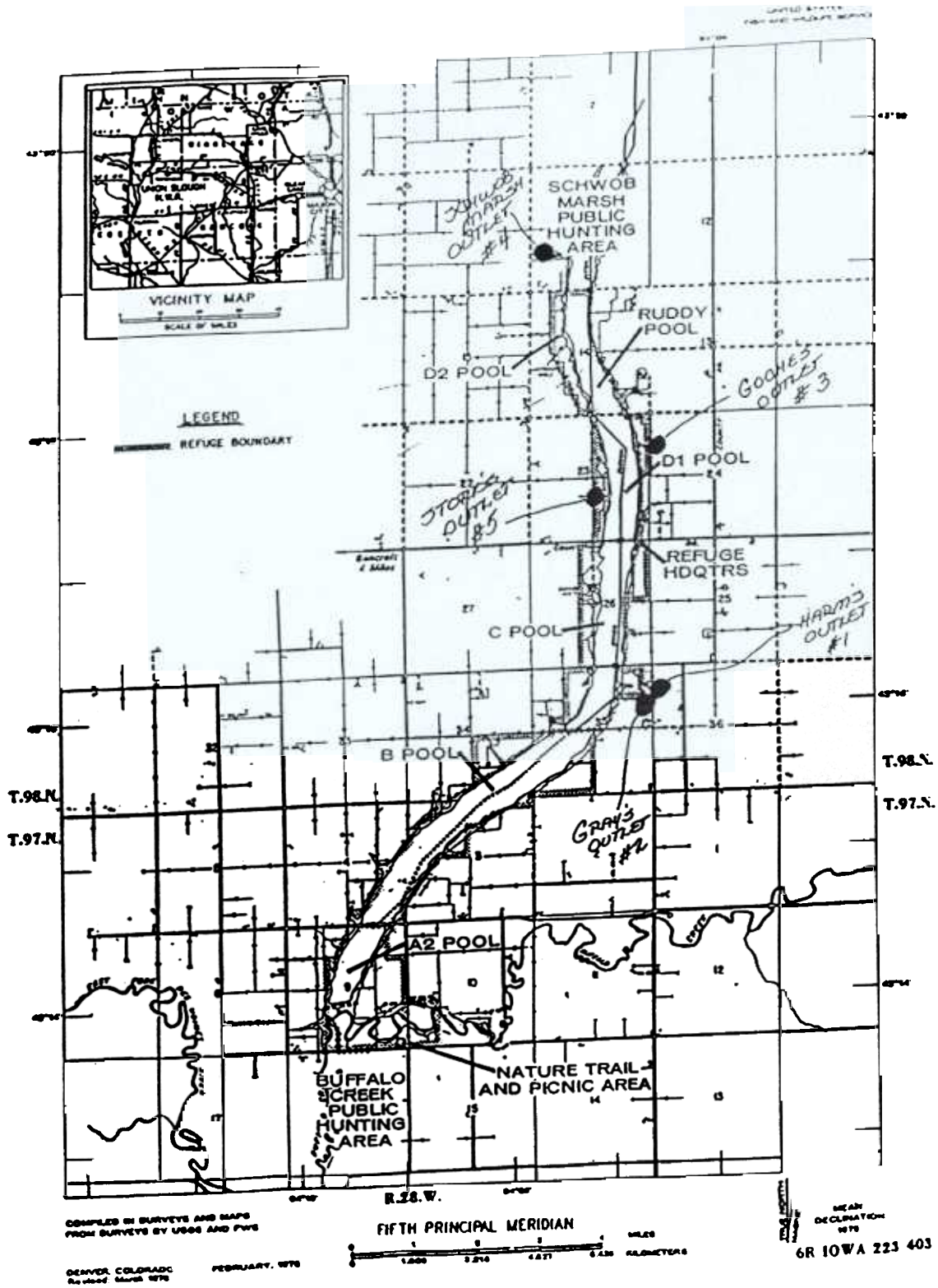

Figure 1. Map of Union Slough National Wildlife Refuge showing sampling locations for the 1990 and 1991 contaminants study.

In June of 1991, samples of sediment were taken at three outlet sites in Union Slough. The samples were placed into chemically clean glass jars and frozen prior to residue analysis. Sediments which were to be analyzed for ammonia were shipped to IHL. These samples were not frozen. IHL protocol is that samples be chilled but not frozen.

Ammonia nitrogen, nitrate nitrogen and pH were analyzed at IHL. Residue analyses for metals and organophosphorus pesticides were performed by the Patuxent Analytical Control Facility in Laurel, Maryland. All other organic analyses were performed by the Mississippi State Chemical Laboratory in Mississippi State, Mississippi.

All of the residue analyses were performed following quality assurance quality control methods established by the Fish and Wildlife Service. IHL used tests approved by the Environmental Protection Agency (EPA).

There were no bioassays performed during this phase of the study

RESULTS

1990

Ammonia concentrations were comparatively low in the water column samples at all of the outlet sites. No minnow mortality was experienced during the 48 hour water bioassays. Results of the water bioassays are found in Table 1.

The 1990 sediment analysis indicated elevated ammonia concentrations at Gray's Outlet and Stork's Outlet of 17.0 mg/L and 15.8 mg/L respectively. These values were 3 to 4 times the concentrations discovered at the other three outlets. Results of 48 hour larval fathead minnow bioassays conducted on sediments from these two sites showed 50% and 96% mortality respectively. These results are displayed in Table 2.

1991

Sediment analysis for ammonia showed elevated ammonia concentrations of 13 to 17 mg/kg at Harm's Outlet. Gray's and Stork's Outlets revealed ammonia nitrogen concentrations of 1.7 to 3.7 mg/kg. For complete results of this analysis see Table 3.

Table 1 Results of 1990 water bioassays from five outlets at Union Slough National Wildlife Refuge (mg/L).

SITE/PARAMETER	Harm's Outlet	Gray's Outlet	Goche's Outlet	Schwob Marsh Outlet	Stork's Outlet
NH_3 - N (start/end)	0.2/1.0	0.2/0.3	0.2/0.2	<0.1/0.20	<0.1/0.2
Total NH_3 (start/end)	0.24/1.2	0.24/0.36	0.24/0.24	<0.12/0.24	<0.12/0.24
Unionized NH_3 (start/end)	<0.01/0.22	<0.01/0.06	0.01/0.05	<0.01/0.05	<0.01/0.05
Total Hardness (as $CaCO_3$)	394	425	393	414	485
Specific conductance (micromhos)	810	900	820	890	1,000
Total alkalinity	188	234	186	200	215
Temperature (°C)	24/24/25	24/24/25	24/24/25	24/24/25	24/24/25
D.O. (initial/24h/48h)	9.1/7.8/7.6	9.3/7.8/7.6	9.2/7.6/7.6	9.4/7.2/7.7	9.2/7.8/7.7
pH (initial/24h/48h)	7.9/8.5/8.6	7.9/8.6/8.5	8.0/8.6/8.6	7.8/8.5/8.6	7.8/8.6/8.6
Total 48 hr Fathead minnow mortality (# dead/# tested)	0/20	0/21	0/21	0/20	0/20

Table 2. Results of 1990 sediment bioassays from five outlets at Union Slough National Wildlife Refuge (mg/L).

SITE/PARAMETER	Gray's Outlet	Harms Outlet	Harms Outlet A	Goche's Outlet	Schwob Marsh Outlet	Stork's Outlet
NH_3 - N (start/end)	14/3.0	3.3/2.6	3.5/2.7	1.0/0.6	1.5/<0.1	13/5.8
Total NH_3 (start/end)	17.0/3.6	4.0/3.2	4.3/3.3	1.2/0.7	1.8/<0.02	15.8/7.0
Unionized NH_3 (start/end)	0.30/0.24	0.11/0.59	0.15/0.61	0.03/0.13	0.06/<0.02	0.44/1.1
Total Hardness (as $CaCO_3$)	234	166	183	251	216	425
Specific conductance (micromhos)	300	280	280	330	310	940
Total alkalinity	160	155	160	190	110	220
Temperature (°C)	25/25/25	25/25/25	25/25/25	25/25/25	25/25/25	25/25/25
D.O. (initial/24h/48h)	5.7/7.6/7.7	4.3/7.5/7.9	4.5/7.7/8.0	4.5/7.7/8.1	4.5/7.8/8.0	5.5/7.5/7.8
pH (initial/24h/48h)	7.5/8.5/8.1	7.8/8.5/8.6	7.8/8.7/8.6	7.6/8.6/8.6	7.8/8.6/8.6	7.7/8.6/8.5
Total 48 hr Fathead minnow mortality (# dead/# tested)	10/20	0/20	0/20	0/20	0/20	20/21

Table 3. Results of 1991 sediment analysis of ammonia from three outlets at Union Slough National Wildlife Refuge (mg/kg).

SITE/PARAMETER	Gray's Outlet - A	Gray's Outlet - B	Stork's Outlet - A	Stork's Outlet - B	Harm's Outlet - A	Harm's Outlet - B
NH_3 - N	1.7	3.2	3.4	3.7	17	13
Nitrate nitrogen	0.4	0.4	1.7	1.4	0.6	0.7
pH	7.7	7.7	7.7	7.6	7.4	7.2

The organic analyses detected no organochlorine insecticides, no organophosphorus pesticides and no chlorophenoxy acid herbicides in the sediments at any of the sampling sites. There were five polynuclear aromatic hydrocarbons (PAHs) detected during the 1991 analysis. Of the three sites sampled, Harm's Outlet had the highest concentrations at 0.06 ppm total PAH. Results from all of the organic analyses are shown in Table 4.

Table 4. Results of 1991 organic analysis of sediments from three outlets at Union Slough National Wildlife Refuge (ppm).

SITE/PARAMETER	Gray's Outlet - A	Gray's Outlet - B	Stork's Outlet - A	Stork's Outlet - B	Harm's Outlet - A	Harm's Outlet - B
Organochlorine pesticides	ND*	ND	ND	ND	ND	ND
Organophosphate pesticides	ND	ND	ND	ND	ND	ND
Chlorophenoxy acid herbicides	ND	ND	ND	ND	ND	ND
Naphthalene (ppm)	ND	ND	ND	ND	ND	0.01
Phenanthrene	0.01	ND	ND	ND	0.01	0.04
Fluoranthrene	0.01	0.02	ND	0.01	0.01	0.01
Pyrene	ND	0.01	ND	ND	ND	ND
Benzo(b) fluoranthrene	ND	0.01	ND	ND	ND	ND

* Not Detected

Metal analysis was performed on sediments collected in 1991. There are six metals which are elevated per the EPA guidelines for sediments (U.S. Environ. Prot. Agency 1977). At Stork's and Harm's Outlet arsenic concentrations were 5.1 and 5.5 ppm respectively. Barium

concentrations ranged from 107 ppm to 224 ppm at all three outlet sites. Iron concentrations at Harm's Outlet were 20,000 ppm. Manganese concentrations at Harm's Outlet site were 395 ppm; at the Stork's Outlet site the concentration of manganese was 1000 ppm. Zinc was present at the Harm's Outlet site at 104 ppm. The results of the metal analysis are displayed in Table 5.

Table 5. Results of 1991 inorganic analysis of sediments from three outlets at Union Slough National Wildlife Refuge (ppm dry weight).

	Gray's Outlet - A	Gray's Outlet - B	Stork's Outlet - A	Stork's Outlet - B	Harm's Outlet - A	Harm's Outlet - B
Aluminum	4430	5370	8230	5540	11700	17700
Arsenic	1.3	1.3	5.1	4.8	4.5	5.5
Barium	148	169	121	107	197	224
Beryllium	0.3	0.3	0.37	0.31	0.6	0.7
Boron	3	3	4	3	6.5	9.7
Cadmium	0.3	0.4	0.3	0.4	0.6	0.6
Chromium	6.9	8	12	8.6	17	23
Copper	6.8	7.4	8.5	7.4	17	18
Iron	11900	11300	10800	8910	16400	20000
Lead	6	6	7	7	12	12
Magnesium	3100	3340	3830	3350	6390	6880
Manganese	226	236	998	1000	383	395
Mercury	0.03	0.03	0.03	0.02	0.054	0.048
Molybdenum	< 1	< 1	< 1	< 1	< 1	< 1
Nickel	8.3	8.7	14	12	17	18
Selenium	0.4	0.4	0.5	0.62	1.8	1.9
Strontium	97.5	111	24.2	21.1	83.9	85.7
Vanadium	7.5	10	24	18	26	42.2
Zinc	34.9	38	45.5	37.2	91.7	104

Four metals met or exceeded the Ministry of Ontario Lowest Effect Level (Jaagumagi 1992). This level is defined as a level of sediment contamination at which the majority of benthic organisms are unaffected. A Severe Effect Level is a level that would be detrimental to a majority of benthic species (Jaagumagi 1992). Table 6 compares three sources of published effects levels for 12 metals. The Ministry of Ontario Lowest Effect Levels appear to be the most sensitive.

The metals which meet or exceed the Ministry of Ontario Lowest Effect Levels are cadmium, copper, nickel and manganese. Cadmium was detected at the Harm's Outlet site at 0.6 ppm. Copper at this same site was detected at 18 ppm. At the Harm's Outlet site, nickel concentrations were 18 ppm. The concentration of manganese at Stork's Outlet site, as previously noted, was 1000 ppm.

Table 6 Effects levels of selected metals (ppm)

	Long and Morgan (1991)			EPA (1977)		Jaagumagi (1992)	
	ER-L[a]	ER-M[b]	AET[c]	MOD[d]	HEAVY[e]	LEL[f]	SEL[g]
Antimony	2	25	3.2	-	-	-	-
Arsenic	33	85	57	3	>8	6.0	33
Barium	-	-	-	20	>60	-	-
Cadmium	5	9	5	-	>6	0.6	10
Chromium	80	145	260	25	>75	26	110
Copper	70	390	310	25	>50	16	110
Iron	-	-	-	17000	>25000	21,200	43,766
Lead	35	110	300	40	>60	31	250
Manganese	-	-	-	300	>500	460	1100
Mercury	0.15	1.3	2.1	-	≥1	0.2	2.0
Nickel	30	50	49	20	>50	16	75
Zinc	120	270	260	90	>200	120	820

a Effects Range - Low
b Effects Range - Moderate
c Apparent Effects Threshold
d Moderately Polluted
e Heavily Polluted
f Lowest Effect Level
g Severe Effect Level

DISCUSSION

The presence of a contaminant does not always correlate to its bioavailability to fish and wildlife resources. There are many different factors to take into account. Alkalinity or acidity may render a contaminant innocuous or increase its toxicity. The presence of other elements which may bond to these contaminants may also affect the level of their toxicity.

Ammonia

Ammonia appears to be the contaminant of primary importance at the Union Slough National Wildlife Refuge. Discussions with the refuge manager lead to the discovery that there is a dairy operation and a hog processing plant in the vicinity of the outfalls having high larval fathead minnow mortality. These businesses may be contributing to the ammonia concentrations found in the sediments.

The agricultural practices in the area are unknown at this time. If corn is planted near the drainages, the common practice of applying anhydrous ammonia to this crop may also affect ammonia concentrations in the sediments near these outfalls. Runoff from the field may also contribute to the ammonia problem. Contributing factors such as depleted dissolved oxygen should be examined in future studies.

Metals

Five of the metals found represent concentrations considered moderately to heavily polluted as established by the EPA (U.S. Environ. Prot. Agency 1977). Three additional metals were found to meet or exceed the Lowest Effect Level demonstrated by the Ontario Ministry of the Environment (Jaagumagi 1992).

The acute toxicity established during the bioassays does not prove or disprove possible effects by metals. To prove this an array of tests may be necessary. Tissue analysis of benthic invertebrates and fish, as well as benthic diversity, may give an indication of the effects of contaminants. Microtox bioassays are more sensitive to certain metals than other organisms, and less sensitive to many organic compounds (Giesy et al. 1988). The addition of Microtox assays in future studies may provide an indicator of metal toxicity.

Organics

There were few organic compounds detected in the sediment samples. Of the four families of compounds analyzed only PAHs were found. The level of total PAH is substantially below the effects range-low concentration determined by Long and Morgan (1991) and should have no effect on fish and wildlife resources at these sites.

CONCLUSION

Eight metals were detected at concentrations of concern at three agricultural drainage outlet sites at the Union Slough National Wildlife Refuge. These metals include arsenic, barium, cadmium, copper, iron, manganese, nickel and zinc. The concentrations of ammonia were elevated in at least one site during each year of this two year study, as determined by toxicity bioassays. Data from the 1990 sampling indicated high bioassay mortality of larval fathead minnows, apparently caused by high concentrations of ammonia. There were no bioassays performed in 1991, but concentrations of ammonia were also elevated during this period.

RECOMMENDATIONS

It is recommended that contaminant impacts at this refuge be studied further. Future investigations should include the following.

1. Survey the area agriculture and farming practices to determine possible impacts. The survey should include types of operations present; what pesticides, herbicides and fertilizers are used; and rates and times of application.

2. The same outlets from the 1990 and 1991 study should be sampled. Sediment and water bioassays should be performed every year, including Microtox assays. The Microtox assays would be used to determine possible effect of metals on benthic organisms. Sediment and water analyses for metals, ammonia and organic compounds should also be performed every year of the study. Samples should not be composited. Each outfall should have a minimum of two distinct sampling locations.

3. Run off from a post application rainfall event should be analyzed.

4. Tissue analysis of fish and benthic diversity should also be studied for the presence of metal and organic pollutants.

5. Rainwater, collected in rain gauges, should be analyzed to determine background concentrations of agricultural products which may be expected to occur in Union Slough.

LITERATURE CITED

Giesy, John P., Robert L., Graney, John L. Newsted, Cornell J. Rosiu, Ann Benda, Russell G. Kreis, Jr. and Frank J. Horvath. 1988. Comparison of Three Sediment Bioassay Methods Using Detroit River Sediments. Environmental Toxicology and Chemistry, Vol. 7.

U.S. Environmental Protection Agency. 1977. Guidelines for the Pollutional Classification of Great Lakes Harbor Sediments.

Jaagumagi, R. 1992. Development of the Ontario Provincial Sediment Quality Guidelines for Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Nickel and Zinc. Water Resources Branch, Ontario Ministry of the Environment.

Long, Edward R. and Lee G. Morgan. 1991. The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program. U.S. Dept. Commerce, NOAA., NOAA Technical Memorandum NOS OMA 52.